NAREL Standard Operating Procedure For Preparing Water Samples for Radium-226 and Radium-228 Analysis

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AMS/SOP-2

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1.0 PURPOSE

1.1 This document describes a method to prepare water samples for determining the activity concentrations of ^{226}Ra and ^{228}Ra.

2.0 SCOPE AND APPLICATION

2.1 This method is suitable for use with water samples. Solid samples are prepared first following the *NAREL Standard Operating Procedure for Preparing Solid Samples for Radium-226 and Radium-228* (AMS/SOP-1) and then with this SOP beginning with Step 10.6. Samples are further prepared for analysis using *NAREL Standard Operating Procedure for Measuring Radium-228 in Environmental Matrices* (AM/SOP-13).

2.2 The detection and quantification capabilities of the preparation and analysis methods are functions of sample size, interferences, instrument backgrounds, detection efficiency, and counting time. The actual MDA for each sample may be different based on any of these variables. For clean water samples, using a 1 L aliquant, a minimum detectable activity (MDA) of 1 pCi/L for ^{228}Ra are obtainable.

2.3 In this method, radium isotopes are separated from other species in the solution by coprecipitation with barium as a sulfate and then as a phosphate. For ^{228}Ra analysis, the precipitate is poured into a beaker and the procedure continues with *NAREL Standard Operating Procedure for Analysis of Radium-228 in Environmental Matrices* (AM/SOP-13).

2.4 Interferences

2.4.1 There are no expected interferences.

3.0 DEFINITIONS

3.1 **assay batch** – a set of test sources prepared by one analyst at the same time, following one analytical method, and delivered to the nuclear counting laboratory for the same nuclear counting procedure.

3.2 **CERLS** – Center for Environmental Radioanalytical Laboratory Science, formerly the Monitoring and Analytical Services Branch (MASB) – the Center at NAREL responsible for analyzing samples for radioactive constituents and hazardous chemicals.

3.3 **control chart** – a graph for monitoring the outputs of a process, such as an analytical measurement process, for the purpose of detecting conditions or trends adverse to quality.

3.4 **laboratory control sample (LCS)** – an artificial sample generated by the analyst in the laboratory and spiked with a known amount of one or more analytes. After being spiked, the LCS is prepared and analyzed in the same manner as a normal sample, and the result of the measurement is compared to the known amount of analyte added to assess the bias of the measurement process.

3.5 **LIMS** – acronym for Laboratory Information Management System – a database and software system used to manage laboratory data, monitor work processes, and produce reports.

3.6 **matrix spike (MS)** – an artificial sample generated by the analyst in the laboratory. An aliquant is taken from one sample at the same time another aliquant is taken for normal preparation and analysis. The second aliquant is spiked with a known amount of one or more analytes. After being spiked, the MS is prepared and analyzed in the same manner

as a normal sample, and the result of the measurement is compared to the unspiked aliquant to assess the effect of the matrix on the performance of the analytical method.

3.7 **method blank** – an artificial sample generated by the analyst in the laboratory, which is as free as possible of the analyte of interest. The method blank is prepared and analyzed in the same manner as a normal sample and alongside real samples, so that the result of the measurement may be used to assess low-level bias in the measurement process, such as that caused by contamination of reagents, as well as cross-contamination of samples.

3.8 **MSDS** – acronym for Material Safety Data Sheet, a document that contains information on the potential health effects of exposure to chemicals or other potentially dangerous substances, and on safe working procedures workers should adhere to when handling chemical products.

3.9 **NAREL** – National Air and Radiation Environmental Laboratory.

3.10 **NIST** – acronym for National Institute of Standards and Technology, formerly the National Bureau of Standards (NBS), which is the national standards body for the United States and a member organization of the International Organization for Standardization (ISO).

3.11 **R value** – the ratio of observed activity divided by the actual amount of added activity, a measure of recovery.

3.12 **replicate sample (duplicate)** – an aliquant taken from one sample at the same time another aliquant is taken for normal preparation and analysis. Both aliquants are prepared and analyzed in the same manner. The analytical result for the second aliquant is compared to the result of the first aliquant to assess the precision of the measurement process.

3.13 **SOP** – acronym for standard operating procedure, a document that describes in detail the steps for performing a routine task.

4.0 EQUIPMENT AND SUPPLIES

4.1 Metricel DM-800 membrane filter, 25 mm dia., 0.8 µm pore size or equivalent.

4.2 Kontes filter funnel, Kontes Glass Co., Vineland, NJ.

4.3 Suction filter apparatus for 25 mm membrane filter.

4.4 Pleated filter paper, Whatman 2V, 32 cm.

4.5 Platinum crucibles, 20 to 30 mL and lids.

4.6 Crucible tongs for platinum.

4.7 Assorted glassware.

4.8 Meker burner.

4.9 Magnetic stirrer and stirring bars.

4.10 Hot plate.

4.11 Hot water bath.

4.12 Emanation storage tubes: Pyrex brand glass tubing, 15 mm i.d. and 45 cm length.

4.13 Analytical balance.

4.14 Top-loading balance.

5.0 REAGENTS AND STANDARDS

5.1 Acetone (CH_3COCH_3) (CAS: 67-64-1). Reagent grade.

5.2 Ethanol (C_2H_5OH) (CAS:64-17-5). Reagent grade.

5.3 Acetone-ethanol mixture (CH_3COCH-CH_2CH_2OH). 50 % each by volume.

5.4 Ammonium sulfate [$(NH_4)_2SO_4$] (CAS:7783-20-2).

5.5 Ammonium sulfate [$(NH_4)_2SO_4$] 10 %. Dissolve 10 g $(NH_4)_2SO_4$ in 90 mL of deionized water.

5.6 Barium chloride ($BaCl_2 \cdot 2H_2O$) (CAS: 10361-37-2).

5.7 Barium chloride ($BaCl_2 \cdot 2H_2O$) stock solution, 10 mg/mL Ba^{+2}. Dissolve 17.79 g $BaCl_2 \cdot 2H_2O$ in 1 L of deionized water.

5.8 Barium chloride ($BaCl_2 \cdot 2H_2O$) dilute solution, 2 mg/mL Ba^{+2}. Dilute 200 mL of the barium chloride stock solution to 1 L in a volumetric flask with deionized water.

5.9 Hydrochloric acid (HCl), 12 M (CAS: 7647-01-0). Reagent grade.

5.10 Hydrochloric acid (HCl), 3 M. Dilute 250 mL 12 M HCl to 1 L with deionized water.

5.11 Hydrofluoric acid (HF), 29 M (CAS: 7664-39-3). Reagent grade.

5.12 Phosphoric acid (H_3PO_4), 15 M (CAS: 7664-38-2). Reagent grade.

5.13 Sulfuric acid (H_2SO_4), 18 M (CAS: 7664-93-9). Reagent grade.

5.14 Sulfuric acid (H_2SO_4), 0.05 M. Dilute 2.8 mL of 18 M H_2SO_4 to 1 L with deionized water.

5.15 NIST-traceable spiking solution containing 12 – 20 pCi/mL of ^{226}Ra.

5.16 NIST-traceable spiking solution containing 12 – 20 pCi/mL of ^{228}Ra.

5.17 NIST-traceable standard solution containing 50 – 100 pCi/mL of ^{228}Ra.

6.0 SAFETY

6.1 Unnecessary or prolonged exposure to laboratory chemicals should be avoided.

6.2 Hydrofluoric acid is a highly reactive chemical. It must be stored in plastic containers, and away from light, heat, and strong bases. HF is highly destructive to tissue and may be fatal if inhaled, swallowed, or absorbed through the skin. HF should be used only by persons trained and familiar with appropriate safety precautions.

6.3 Material Safety Data Sheets (MSDS) are available to all personnel involved in chemical analysis. It is the responsibility of the analyst to be familiar with chemicals used during an analysis.

6.4 Refer to the *NAREL Chemical Hygiene Plan* for verification of appropriate safety and health practices.

7.0 ROLES AND RESPONSIBILITIES

7.1 Unless otherwise noted, the radiochemist is responsible for performing all steps of this procedure. These responsibilities include grouping samples into QC batches, performing chemical separations and recording all data in a laboratory notebook.

7.2 The NAREL QA Chemist is responsible for preparing ^{226}Ra and ^{228}Ra spiking solutions.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Water samples can be shipped to the laboratory and stored in either glass or plastic. No refrigeration is required.

8.2 Nitric acid should be added to the water samples in the field to bring the pH to less than 2. Upon receipt of the samples, NAREL staff checks the pH of each water sample for radium analysis, and adjusts the pH as necessary.

8.3 Samples must be stored in a safe and secure environment to maintain chain of custody.

9.0 CALIBRATION AND STANDARDIZATION

9.1 The procedures for preparing calibration sources are described in *NAREL Standard Operating Procedure for Measuring Radium-228 in Environmental Matrices* (AM/SOP-13).

9.2 The NAREL QA Chemist prepares the ^{226}Ra and ^{228}Ra standard and spiking solutions by diluting certified NIST-traceable standards gravimetrically to an appropriate activity. The diluted standard and spiking solutions are maintained in the NAREL QA laboratory and distributed to analysts as needed.

10.0 PROCEDURE

10.1 If requested by the client, or if the water sample contains high suspended solids, the sample can be filtered using a1 L aliquot through a pleated filter paper. Save any solids if the radium content of the solids is needed. The solids are prepared using NAREL Standard Operating Procedure for *Preparing Solid Samples for Radium-226 and Radium-228 Analysis* (AMS/SOP-1).

10.2 Prepare quality control (QC) samples to be processed and analyzed with the field samples. See section 11 for required QC samples.

10.2.1 If the sample is to be analyzed for ^{228}Ra, prepare a standard to be run with the assay batch.

10.2.1.1 The chemical yield determined for the standard (spiked sample) is assumed to be equal to the yield of the unknown samples. The standard must be analyzed in the exact manner and at the same time as the unknown sample.

10.2.1.2 Add 1000 mL of DI water to a 2 L beaker. Add 1.0 mL of the standard spike solution and mix well.

10.2.1.3 Proceed with Step 10.3 for the standard, QC samples, and field samples.

10.3 Place each 1000 mL water sample in a 2 L beaker, add a magnetic stirring bar and place on a stirrer. If the sample does not contain 1000 mL, add the measured sample and add DI water to make a 1000 mL volume. In a fume hood, add the following to the water sample with stirring: 20 mL of 12 M HCl; 50 mL of dilute $BaCl_2$ solution; and 20 mL of 18 M H_2SO_4.

10.4 Cover the sample and allow it to stir for a minimum of 90 min to precipitate $BaSO_4$.

10.5 Remove the magnetic stirring bar and allow the mixture to precipitate overnight.

10.6 Decant the clear liquid off the top so that the entire quantity does not require filtering.

10.7 Transfer the remaining liquid and precipitate to a filter funnel (with membrane filter) attached to suction. Using 0.05 M H_2SO_4, wash the beaker and filter funnel.

10.8 Remove the clamp and lift the filter funnel carefully. Use a membrane filter to remove any precipitate on the bottom of the filter funnel and place in a platinum crucible.

10.9 Carefully remove the membrane filter with precipitate from the filter apparatus and place it in the platinum crucible used in step 10.8.

10.10 Add 25 drops (about 1 mL) of 29 M HF and 0.3 mL of 10 % $(NH_4)_2SO_4$ solution to volatilize, as SiF_4, any silica that may be present.

10.11 Place the crucible on a hot plate at low temperature and heat to dryness.

10.12 Remove crucible from hot plate. Add 2 mL of acetone-alcohol mixture, ignite with a match, and burn off the solvents.

10.13 Put the top on the crucible, place it on a tripod over a Meker burner, and heat until the filter paper is ashed completely (about 5 – 10 min).

10.14 Remove top from crucible and remove from the heat. Add 1 mL of 15 M H_3PO_4.

10.15 Place the crucible on a hot plate at low setting for 15 min. Turn hot plate up to a higher temperature for an additional 15 min or until milky white slurry develops.

10.16 Remove crucible from hot plate and hold the crucible with platinum-tip tongs in the hottest part of the Meker burner flame, swirl the covered crucible.

10.17 When the white solids dissolve and the bubbling and fumes decrease, swirl the crucible in the upper part of the flame for 1 min. The result is a clear melt.

10.18 Fill the crucible 1/4 inch from the top with 3 M HCl.

10.19 With the lid off, place the crucible in a hot water bath, and allow 3 M HCl to evaporate slowly (usually takes from 1.5 to 3 hours) until abundant white crystals remain.

10.20 Fill the crucible approximately half full with deionized H_2O and allow the crystals to dissolve.

10.21 Pour the liquid into a 100 mL beaker and continue with *NAREL Standard Operating Procedure for Measuring Radium-228 in Environmental Matrices* (AM/SOP-13).

11.0 QUALITY CONTROL PROCEDURES

11.1 Reference standards used to provide spiking solutions, standards, or calibration sources must be obtained from the National Institute of Standards and Technology (NIST) or suppliers who participate in supplying NIST standards or NIST traceable radionuclides.

11.2 For each QC batch of up to 20 samples of the same matrix, the analyst must add the following QC samples:

11.2.1 method blank

11.2.1.1 The analyst prepares the method blank by adding 1 L of DI water to a beaker and continuing with step 10.3 of this procedure

11.2.2 laboratory control sample (LCS)

11.2.2.1 The activity of the LCS must be at least five times the normal expected minimum detectable activity (MDA) and should be comparable to sample activities when sample activities in the batch are expected to be higher than five times the MDA. The spike level should be high enough to ensure that under expected measurement conditions, the relative standard counting uncertainty will not exceed 5 %.

11.2.2.2 The analyst prepares the LCS by adding 1.0 mL of spiking solution to a beaker containing 1 L of DI water and continuing with this procedure at step 10.3.

11.2.3 replicate sample (duplicate)

11.2.4 matrix spike

11.3 Analysts are required to control chart results from blanks, and to observe the control charts for indicators of possible problems in the measurement system. LIMS software allows the analyst to input data points and to view and print the control charts.

11.4 See the *NAREL Radiochemistry Quality Assurance Manual* for acceptance criteria for QC samples and equations for calculating values for quality indicators.

11.5 Failure of a QC analysis requires that the analyst or the first person who discovers the failure initiate a corrective action report.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Refer to *NAREL Standard Operating Procedure for Measuring Radium-228 in Environmental Matrices* (AM/SOP-13).

13.0 DATA REVIEW

13.1 Refer to *NAREL Standard Operating Procedure for Measuring Radium-228 in Environmental Matrices* (AM/SOP-13).

14.0 METHOD PERFORMANCE

14.1 Refer to *NAREL Standard Operating Procedure for Measuring Radium-228 in Environmental Matrices* (AM/SOP-13).

15.0 POLLUTION PREVENTION

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution

prevention exist in laboratory operation. The EPA places pollution prevention as the management option of first choice.

15.2 Volumes of prepared reagents are made in the smallest amounts consistent with sample batch sizes to minimize having to discard unused reagents.

16.0 WASTE MANAGEMENT

16.1 The EPA requires that laboratory waste management practices be consistent with all applicable rules and regulations. It is the responsibility of each laboratory to assure adherence to EPA regulations.

16.2 Waste streams generated by this procedure for each sample include the following: 20 mL hydrochloric acid, 20 mL sulfuric acid, and the filtrate from the original sample.

16.3 The analyst disposes of the waste by neutralizing it and pouring it down the drain.

17.0 REFERENCES

17.1 *NAREL Chemical Hygiene Plan*.

17.2 *NAREL Radiochemistry Quality Assurance Manual* (QA/QAM-1).

17.3 *NAREL Standard Operating Procedure for Preparing Solid Samples for Radium-226 and Radium-228* (AMS/SOP-1).

17.4 *NAREL Standard Operating Procedure for Document Control* (QA/SOP-1).

17.5 *NAREL Standard Operating Procedure for Measuring Radium-228 in Environmental Matrices* (AM/SOP-13).

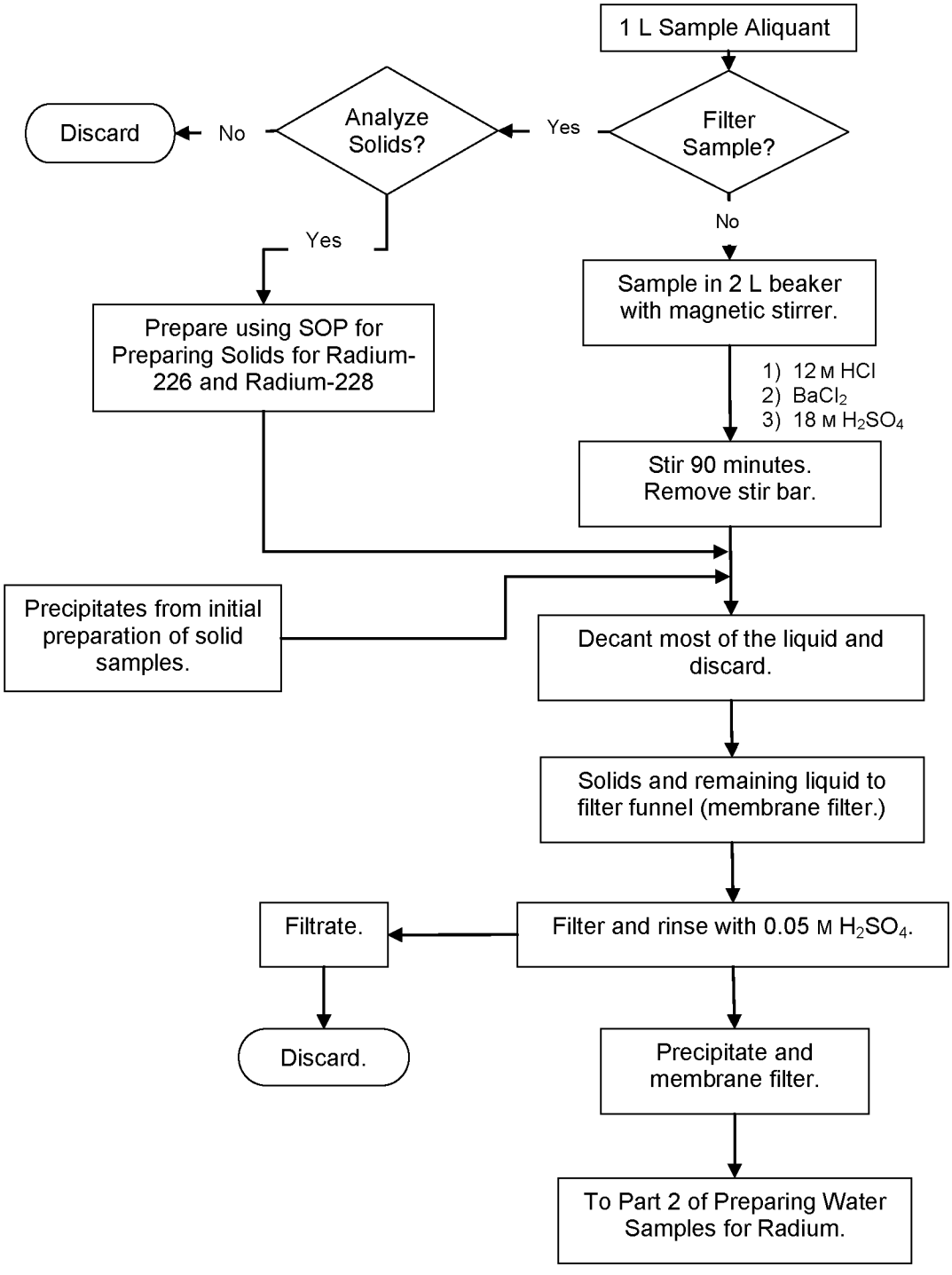
18.0 APPENDICES (TABLES, DIAGRAMS, AND FLOWCHARTS)

18.1 Radium-226 and Radium-228 Water Preparation – Part 1

18.2 Radium-226 and Radium-228 Water Preparation – Part 2

Appendix 18.1

Radium-226 and Radium-228 Preparation for Water Samples – Part 1



Appendix 18.2

Radium-226 and Radium-228 Water Sample Preparation – Part 2